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MODIFICATION OF ALKALI-FREE GLASS COMPOSITIONS FOR FIBERGLASS PRODUCTION

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An alkali-free boron-free glass fiber composition is developed which in its main characteristics surpasses fiber of type E. The fiber based on the developed glass composition is recommended as a filler for high-strength glass plastics which can operate under the long-term effect of aggressive media. The technological parameters of the developed composition make it possible to produce the fiber on available machinery.

The requirements imposed on the service properties of glasses used in fiberglass production in general can be reduced to high strength and chemical resistance. Besides that, great attention in the production of electric engineering glass fiber is paid to its electrical parameters. The most common industrial fiberglass in Russia and abroad is alkali-free aluminoboron silicate glass of type E which has the following chemical composition (wt.%): 52–56 SiO₂, 12–16 Al₂O₃, 5–10 B₂O₃, 0–1.5 TiO₂, 16–25 CaO, 0–5 MgO, 0–2 (Na₂O + K₂O), 0–0.8 Fe₂O₃, 0–1 F [1].

The standard domestic alkali-free glass and the similar glasses produced abroad have high water resistance (hydrolytic class I), good dielectric properties (volume resistance $10^{14} \Omega \cdot \text{cm}$), sufficiently high strength (up to 2800 MPa), and a low TCLE ($\approx 60 \times 10^{-7} \text{ K}^{-1}$).

Since the electric properties depend on the alkali content, domestic and international specifications usually define glass E based on its alkali content, namely, such glass should not contain more than 1% alkali converted to Na₂O. The Japanese standards limit the alkali content to 0.8%. The actual content of alkalis and the presence of traces of other elements, as a rule, depend on the choice of raw materials. Most glasses contain a small quantity of fluorine, which facilitates the dissolution of raw materials, decreases the temperature of the melt liquidus, and improves the fiber formation. The presence of ferric oxide in the materials also has a substantial effect on the stability of fiber formation, since iron ions increase the rate of infrared radiation absorption of the melt, and the rate of heat released by the glass leaving the spinneret of the glass-melting vessel is accelerated. All glasses used in the production of fiber of type E contain a relatively high (up to 10%) quantity of boron anhydride, which is an expensive component and not easily accessible. The sub-

stantial volatilization of this component in melting has a negative effect on the ambient medium.

The glass composition has a great significance for the chemical resistance and strength of the fiber under the effect of water and steam. E glasses have high chemical resistance to water and high-pressure steam [2]; however, the acid resistance of these fibers is low. For instance, in 3 h 46 wt.% of glass is dissolved under the effect of 2 n. H₂SO₄.

The alkali resistance of aluminoboron silicate fibers is approximately the same as that of some zirconium-free alkaline glasses. Under the effect of 0.1 N NaOH solution for 3 h, 10.5% initial fiber mass passes into the solution, and 50.67% under the effect of 2 N NaOH solution. In this case all glass components dissolve, and the fiber thickness decreases [3].

For a number of years numerous researchers studied modifications of the chemical composition of E-glasses, which was prompted by the need for solving various technological, ecological, and economic problems. Thus, a significant technological disadvantage of the initial E-glass composition was the high aggressiveness of the melt with respect to refractory material, which soon corroded at a relatively low melting temperature. This circumstance not only substantially reduced the furnace campaign period, but enriched the glass composition with refractory components, primarily, zirconium oxide, in the case of using zirconium-boron refractories. As a result, the temperature of the upper crystallization boundary increased and, accordingly, the risk of glass crystallization during the fiber formation became higher. This problem was solved by the development of glass composition 10 (Table 1) known as glass 621, which is distinguished by an increased CaO content due to the exclusion of MgO. Later the implementation of corrosion-resistant refractories in glass fiber production made it possible to resume using magnesium-bearing compositions and increase the melting temperature to 1600°C.

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TABLE 1

Composition	Weight content, %									Published source
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	MgO	ZnO	Na ₂ O	TiO ₂	BaO	
1	53.0	15.0	10.0	17.0	4.0	—	0.5	—	—	[4]
2	54.0	13.5	—	18.5	1.5	2.0 SrO	1.5 MnO ₂	6.0	3.0	USSR Inv. Certif. No. 141273
3	54.3	8.7	—	13.8	3.3	16.9 SrO	1.1 Fe ₂ O ₃	0	1.8	USSR Inv. Certif. No. 178458
4	55.5	16.0	—	14.0	8.0	—	0.5	6.0	—	[4]
5	54.0	15.0	4.0	20.0	2.5	1.5 MnO	0.8	—	2.0	[5]
6	54.0	14.5	8.0	18.0	4.5	—	0.7	—	—	[5]
7	54.0	14.5	6.0	16.0	4.0	4.0	2.0	0	—	[5]
8	68.0	22.0	—	—	10.0	—	—	0	—	[5]
9	54.0	14.0	10.0	17.5	4.5	—	1.0	0	—	U.S. Patent No. 2334961
10	54.0	14.0	10.0	22.0	—	1.4 F ₂	1.0	0	—	U.S. Patent No. 2571074
11	56.0	12.0	5.0	22.0	5.0	—	—	—	—	U.S. Patent No. 2582919
12	58–60	11–13	—	21–23	2–4	—	< 1	1–1.8	—	U.S. Patent No. 4542106
13	60.1	13.2	—	22.1	3.0	—	0.8	0.1	—	U.S. Patent No. 5789329
14	58.0	11.0	—	22.5	2.6	2.6	1.0	2.4	—	Canada Patent No. 1067230
15	55.8	14.8	5.2	21.0	—	—	1.4	—	—	Canada Patent No. 1248555
16	60.0	15.0	—	20.0	5.0	—	—	—	—	Gr. Britain Patent No. 520247
17	52.4	22.4	—	9.1	12.1	0	—	—	—	Netherlands Patent No. 218012
18	54–60	9–14.5	—	17–24	1.5–4	—	—	2–4	—	France Patent No. 2182184
19	54–57	13–16	5–7.5	21–23	0.6–3	—	0–1	0–1	—	France Patent No. 2650268
20	59.0	12.1	—	22.6	3.4	—	0.9	1.5	—	EU Patent No. 0275541

During the last decade, after new laws on environmental safety and protection of the ambient were adopted, many countries have been carrying out research directed at the reduction or complete exclusion of volatile and toxic components (fluorine and boron oxide) from the E glass composition. It is known that when boron-containing glass is melted in a glass melting furnace heated by gas or liquid fuel, up to 10–20% of the boron oxide contained in the batch is emitted into the atmosphere via waste gases. Apart from solving ecological problems, a decreased content or exclusion of boron oxide from the glass composition allows for substantial savings in the fiberglass production cost, since the boron-bearing batch components are the most expensive (their cost amounts to nearly half of the total material cost).

The purpose of the present paper is the modification of alkali-free aluminoboron silicate glass of type E with the aim of reducing or completely eliminating the boron oxide content, as applied to the domestic conditions of glass fiber production.

During the investigation it was taken into account that fiberglass is mostly used to produce power-related fiberglass materials with a long warranty period for storage under conditions of increased humidity. Such materials should have the minimum possible content of R₂O. Electrical engineering consumes large quantities of glass fiber. At the same time, the content of alkali metal oxides in the glass is limited to 1%.

The region taken as the basis for the selection was the region in the SiO₂–Al₂O₃–CaO–MgO system located near the ternary eutectic between the crystallization fields of anorthite, pyroxene, and pseudowollastonite and the boundary lines converging in the eutectic. This region is limited by the following mass contents (%): 54.0–62.0 SiO₂, 10.0–17.0

Al₂O₃, 15.0–24.0 CaO, 2.0–9.0 MgO. The modifying additive was TiO₂. The content of R₂O in the glasses did not exceed 0.5%. It was possible to resume the study of this system, since recently, in the course of developing specialized fiberglass, new methods for glass melting and fiber production were developed, which involve melts of higher viscosity that are more inclined to crystallization than the standard alkali-free aluminoboron silicate glass.

The studies were conducted along the following lines:

- modification of the composition of alkali-free aluminoboron silicate glass: replacement of B₂O₃ by oxides of alkaline-earth elements (CaO and MgO);
- modification of the CaO : MgO ratio;
- introduction of TiO₂ additive;
- study of the technological and physicochemical properties of glasses and glass fibers of the modified compositions;
- optimization of glass compositions to meet preset technological and physicochemical properties.

The studies investigated the melting and working capacity of glasses, their tendency for crystallization, viscosity, capacity for fiber formation, density, and chemical resistance to various reactants and the tensile strength of fibers.

Glasses of more than 30 compositions were melted in platinum crucibles at 1520°C. The criteria for the technological evaluation of glass were the temperature dependence of viscosity and the temperature of the upper crystallization limit t_s . The value t_s and its relationship with viscosity are of special significance in production of fiberglass: this temperature has to be lower than the temperature correlated to the working viscosity. This is why special attention was focused on glasses with the lowest possible upper crystallization limit.

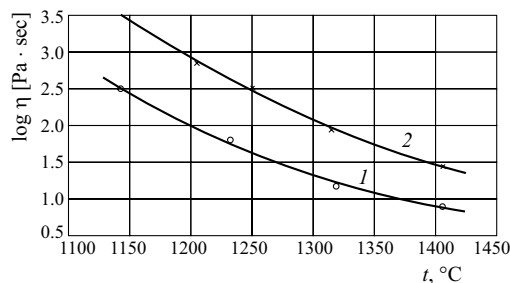


Fig. 1. Temperature dependence of viscosity in glasses E (1) and Kt (2).

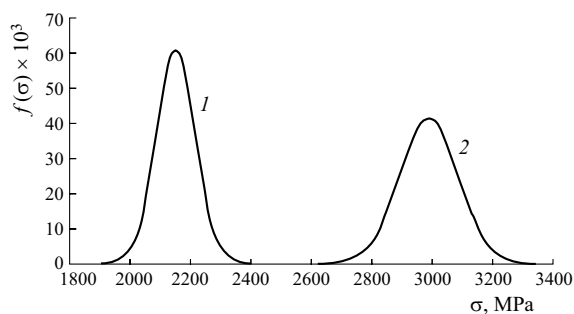


Fig. 2. Tensile strength of glass fiber in compositions E (1) and Kt (2).

The crystallizing properties of all the considered glass compositions are significantly inferior to those of the standard aluminoboron composition. As the B_2O_3 content in the glasses decreased from 10 to 0%, the upper crystallization limit grew from 1140 to 1220°C. A modification of the dolomite ratio and simultaneous introduction of TiO_2 to boron-free glass made it possible to bring t_s down to 1200°C.

As a result of the experiments performed, the composition Kt was optimized with respect to the combination of its working properties (viscosity and the upper limit of crystallization), and glass fiber was produced based on this glass (Fig. 1 and Table 2).

In order to ensure a normal process in production of glass globules and glass fiber, t_s should be below the temperature corresponding to the viscosity 400 Pa·sec ($\log \eta = 2.6$). This is due to the fact that glass globules are molded on an ASSh machine from glass melt supplied from the melt feeder having viscosity of about 400 Pa·sec ($\log \eta = 2.6$), whereas glass fiber is formed from melt of viscosity of about 160–400 Pa·sec ($\log \eta = 2.2–2.6$). For glass Kt, the melt temperature related to $\log \eta = 2.6$ is equal

to 1235°C, and the upper limit of crystallization is 1200°C. The temperature intervals $t_{\log \eta = 2.6} - t_s$ and $t_{\log \eta = 2.6} - t_{\log \eta = 2.2}$, which are equal to 25 and 75°C, respectively, suggest the possibility of producing fiberglass on the available machinery without introducing modifications to the machine design.

A fiber of diameter 10 μm was produced on a single-spinneret laboratory set at the Stekloplastik Association. The drawing was performed at a rotational speed of the reel of 1400 min^{-1} and a temperature of 1310°C. The working properties of Kt-glass allow for stable fiber formation. The tearing strength of the fiber in drawing was satisfactory. The fiber diameter was measured employing a microscope and calculated as the arithmetical mean of 30 measurements.

Since the purpose of the study consisted in the synthesis of glasses suitable for fiber formation with increased chemical and strength parameters, it was interesting to correlate the physicochemical properties of the synthesized alkali- and boron-free glass Kt with the properties of the standard glass E. The investigated properties were glass density, chemical resistance of the fiber to various aggressive media, and the tensile strength of the fiber.

It was found that the acid and alkali resistance exhibited by glass Kt is, respectively, 18 and 1.5 times higher than that of glass E. The glass Kt also surpasses glass E in water resistance by 16% (Table 3).

The mechanical properties of fiberglass are of great significance. This is especially true of the elementary fiber strength, since this parameter to a large extent determines the possibility of textile processing of fiber and the strength of finished goods, which is a determining factor in production of structural glass plastics.

Studies of the mechanical properties of fiberglass demonstrated that glass Kt exceeds glass E in tensile strength (Fig. 2). This can be accounted for presumably by the fact that the fiber formation temperature in glass Kt is higher than in glass E, and at a higher temperature, the glass melt structure in Kt is more homogeneous. If the cooling rate of the fiberglass is high, the fiber retains the structure of the more homogeneous glass melt and contains fewer defects, which have a negative weakening effect on the fiber.

Thus, the most expedient line in the modification of E glasses for the purpose of achieving satisfactory working properties and increased physicochemical and mechanical parameters is the exclusion of boric anhydride from the glass composition at the expense of a higher content of alkaline-

TABLE 2

Glass	t , °C		t_s , °C
	for $\log \eta = 2.2$	for $\log \eta = 2.6$	
E	1215	1165	1140
Kt	1285	1235	1200

TABLE 3

Glass	Weigh loss after boiling for 3 h					
	in H_2O		in 1 N H_2SO_4		in 2 N NaOH	
	mg	%	mg	%	mg	%
E	17.6	0.6	1087.7	38.3	605.8	21.3
Kt	14.8	0.5	60.4	1.8	382.2	11.8

earth metal oxides, as well as small quantities of TiO_2 additive.

The modified boron-free glass compositions have higher viscosity and a higher upper crystallization limit, which calls for higher melting temperatures. The fiberglass has to be produced at higher (by 60 – 80°C) temperatures.

The elimination of B_2O_3 from the glass E composition and introduction of TiO_2 significantly improve the chemical resistance of the fiberglass to strong acids, raise to some extent its resistance to alkalis, and substantially improve the strength parameters of the elementary fiber. This makes it possible to develop and extensively use corrosion-resistant glass plastics reinforced with such fiber and to use this fiber as a filler for high-strength glass plastics.

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